BASIC INVESTIGATIONS OF CERAMIC FIBRE-ALLOY COMPACTS

FINAL REPORT

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M. M. SKRILL
E. S. MACHLIN
S. WEINIG

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Contributing Personnel: M. M. Skrill
E. S. Machlin
S. Weinig

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47 Buena Vista Avenue
Yonkers, New York

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I. INTRODUCTION:

The objectives of this research were 1) to devise techniques of producing composite materials of non-metallic fibers and metals 2) to test such composite materials with the view of evaluating the factors that affect their strength. These objectives have been achieved.

II. TECHNIQUES OF PRODUCING FIBER-METAL COMPOSITES:

Many techniques of producing non-metallic fiber-metal composites were investigated. Initial attempts to infiltrate uncoated fibers with copper or copper alloys proved that a lack of wetting of the fibers inhibited metal flow. Subsequently, satisfactory compacts were made using a vacuum casting technique and aluminum coated corning E-glass fibres. The technique finally achieved, which is eminently satisfactory, involves the infiltration of coated fibers by molten metals that cannot penetrate the fiber coating. The necessity of having a coating on the fiber that prevents attack by the molten metal but which promotes wetting of the fibers by the molten metal was shown by the results of tests to be described later. Two coatings are especially useful, namely nickel and

molybdenum. Both these metals do not tend to attack silica or more refractory oxides. Hence, they are compatible with most non-metallic fibers including glass fibers. The metals can be deposited on the fibers from the gas phase by thermal decomposition of the metal carbonyls. These metals have high surface energies, hence, they are easily wet by metals having lower surface energy. Molybdenum has the further advantage that its oxide can be easily removed by heating in vacuum. These coatings have distinct advantages over coatings such as aluminum and lead, which have been used in the past, in that the latter coatings react with the fibers and thereby weaken them. This statement will be supported by evidence presented in a later section.

A. RECOMMENDED TECHNIQUE FOR PRODUCING FIBER-METAL COMPACTS.

1. Choose fiber to be coated
2. Coat fiber according to recommended procedure
3. Pack fiber according to desired fiber orientation and volume concentration.
4. Infiltrate with desired metal
5. Cool compact to achieve progressive solidification.

Each of these steps will now be discussed.

Choice of Fiber:

Table 1 lists many, but not all, non-metallic fibers that can be purchased in a form useful for the production of fiber-metal compacts. Most fibers are protected by some organic coating which must be removed. The most desirable procedure of removing such coatings is by combustion. The fiber properties which are useful in determining their choice for a particular application are also presented in Table 1. The fiber strengths shown in this table were determined in this investigation on typical uncoated fibers. The strength was evaluated by measuring the load to failure and the cross-sectional area of fibers supported by adhesive tapes. The gauge length was 1/4 inch. Load was applied by slowly pouring sand into an envelope supported by the fiber. The cross-sectional area of the fracture was measured using a metallograph to magnify the fiber diameter. Each value represents an average of at least five separate measurements. The range in values is about $\pm$ 5%. The other properties (softening temperature, specific gravity, thermal expansion coefficient) were obtained from the literature. It should be noted that because protective coatings are used, the fiber itself can be chosen

without regard to its probable reactivity with the metal matrix. Thus, it is quite likely that the relatively unrefractory material "Fiberfrax" can be used to strengthen iron at elevated temperature providing it is coated with molybdenum.

Coating Procedure:

It is well recognized that glass fibers, when freshly drawn, have strengths in excess of one million pounds per square inch. These fibers are sensitive to damage both from abrasion and from atmospheric attack. Thus, it has been the practise to coat glass fibers with either a starchy substance or a resin to protect them in the course of manufacture of fiber glass-plastic articles. If the fibers, so protected, are to be incorporated into metallic materials, then these organic coatings must be removed from the fibers. However, when this is done the fibers are resensitized with regard to damage in handling and exposure to air.

To avoid the above difficulties, a process was developed that consisted of removal of the organic coating by combustion and subsequent coating with nickel by the thermal decomposition of nickel carbonyl. This entire process can be accomplished without handling or exposure to air. According to this procedure, the fibers should first be heated either in vacuum or flowing

inert gas in order to eliminate adsorbed water vapor and as much oxygen as possible. Coating should be carried out to produce a uniform deposit to a desired thickness. The minimum thickness is in one particular case determined by the need to have coating remain on the fiber without dissolution into the infiltrating metal in the event the coating is soluble in the molten metal but not in the solid metal. The coating may be carried out "in situ" on packed fibers or on loose fibers that will be subsequently packed.

Fiber Packing:

The factors that need to be considered in the packing of fibers are described in Appendix I. As indicated there, fiber orientation is very important for the production of a ductile compact. It is desirable to have the fibers oriented at about 45° to all the principal tensile axis to achieve maximum ductility.

Infiltration:

Infiltration is possible when the surface energy of the infiltrant is less than the surface energy of the coating (oxidized or not as the case may be). The surface energy of the infiltrant may be lowered by solute additions. The surface energy of the coating

may be raised if it is oxidized by reducing the surface oxide. Infiltration is generally very rapid and complete with fiber contents of 5 volume percent or above.

Solidification:

Because "castings" are produced by the infiltration technique it is desirable to have progressive solidification to eliminate microporosity and pipe in the final parts. Standard casting principles can be applied.

III. FACTORS THAT AFFECT THE STRENGTH OF FIBER-METAL COMPACTS:

For fibers that are sufficiently long to prevent fracture around the fiber (along the fiber-metal interface for example) and which are similarly oriented it has been found experimentally in this investigation that the strength of the compact is the volume averaged strength of the two components (Figures 1 and 2). This result agrees with that found by Weeton et al[1] for tungsten fibers imbedded in copper. Thus, two important factors controlling the strength of compacts are the individual strength of the fiber itself and the volume percentage of fiber in the compact. The third factor, which is less important, is the strength of the metal

itself. Analytically, the relation is:

$$S_c = V_f \times S_f + (1-V_f) S_m$$

where S_c = strength of compact

V_f = volume fraction of fiber in compact

S_f = strength of fiber itself

S_m = strength of metal itself.

This relation holds for the case where the deviation of fractional area occupied by fiber along any cross-sectional area in the specimen from the average is small. Thus, it holds best for longitudinally oriented fibers and not at all for transversely oriented fibers where cross-sectional areas exist that do not contain any fiber area at all! The need to have a uniform distribution of fiber area is often not appreciated and the lack of a uniform distribution of fibers has been responsible for many premature failures. To overcome this difficulty all fibers used in this investigation were as long as the specimens except where noted.

Fiber Strengths:

As revealed in Table 1 the strengths of fibers vary markedly. Even for a given fiber the strength is not invariant. Fiber strength is not only a function of handling prior and during incorporation into a composite and atmospheric attack but it is also

affected by possible reaction with the metal which it contacts. This fact was made evident in this research in experiments conducted using aluminum coated E-glass imbedded in an aluminum matrix by infiltration.

The strength of the coated fibers prior to infiltration was found to be about 80,000 psi. From Figure 2 and equation 1 the strength of the fiber in the compact was estimated to be about 40,000 psi. Further, the strength of the fiber was probably reduced from at least the value of 700,000 psi measured on as-received uncoated fibers to about 80,000 psi due to the coating operation alone.

The fact that the method of infiltration and fiber packing did not harm the fiber strength was shown by tests in which fibers were coated by decomposition of the carbonyl with metals that do not tend to react chemically with the fibers and thereafter subjected to the same fiber packing and infiltration technique as for E-glass fibers. In this case, the strength of the fiber, "in situ" as calculated

using equation (1) and measured values of the uncoated fiber strength were found to be the same as the uncoated fiber. This proof was obtained with a tin compact containing "Fiberfrax" fibers. The fiber strength in the nascent state was measured to be 200,000 psi. This value is an average for the third fracture in sequence in a one inch gauge length over ten fibers. The strength of the tin-fiber composite was measured to be 14,000 psi with an elongation of 4%. Since the metal has a strength of 2000 psi, equation 1 predicts a compact strength of 13,800 psi. The results of our few tests in this area imply that protection of fibers at the moment they are produced with coatings of inert metals by vapor deposition (to be called barrier coatings) may provide fibers with their as drawn strengths for incorporation into compacts (the latter strengths may exceed 1,000,000 psi).

Volume Fraction Fibers:

Without difficulty it was found possible to incorporate up to about 20% by volume of fibers into the compact. This amount was achieved using longitudinally oriented fibers. It was apparent, however, that to achieve greater packing density without

harming the fibers it would be necessary to place each fiber into its theoretical position in a perfect packing of cylinders. Further, such perfectly packed brittle fibers would not be likely to yield ductile composites. Thus, much of the work was limited to the volume fractions less than 20%. Within this range the effect of volume fraction on strength was found to be as described in equation 1.

Fiber Length:

It was determined that for short fibers there was little strengthening - on the order of what would be expected from a dispersed hardened phase of the same size and shape as the fibers. Thus, there is little doubt that fiber strengthening is due to the fact that long fibers carry load in the composite. The behavior described by equation (1) can be interpreted in the following way. As load is applied to the composite and the stress in the metal reaches the flow stress, load is transferred to the fibers. The load carried by the metal at any moment equals the product of its flow stress and cross-sectional area. The load carried by the fibers increases until the fracture strength is reached. At this point the fraction of the load carried by the fibers equals

$$\frac{V_f \times S_f}{S_f + S_m}$$

and the fraction carried by the metal equals

$$(1-V_f) \quad \frac{S_m}{S_f + S_m}$$

In this case the stress S_m should equal the flow stress of the metal, whereas as indicated in equation (1) this stress appears to be the "strength" of the metal. The data are too few however to clarify this point. This analysis suggests that it may be worthwhile to investigate this point in future research. That is, it is predicted that S_m should be the flow or yield stress at very small strains.

IV. FACTORS THAT AFFECT THE DUCTILITY OF FIBER-METAL COMPACTS:

When the fibers are oriented parallel to the principal stress axis and the mechanism of strength is as described in equation (1), then no ductility would be expected when the fibers fracture in a brittle manner. This result was obtained. All longitudinally oriented fibers yielded brittle fractures.

In the hope that some elongation could be obtained by allowing fiber rotation prior to fracture and shear strain parallel to the fibers in the metal between the fibers, compacts were made with fibers oriented at about 45° to the tensile axis. Preliminary experiments with such specimens indicated that it was possible to achieve at

least 5% elongation without materially decreasing the tensile strength of the compact. Strangely, the yield strength (0.2%) of the compact appeared to be much higher than for the metal itself. A typical result is shown in Table 2 for a tin matrix containing 6% by volume of fibers having the uncoated strength of 200,000 psi. The work accomplished with this variable is just sufficient to indicate that a more complete study of this area is justified.

SUMMARY OF RESULTS:

1. Aluminum coated E-glass fibers have much lower strength than the prior uncoated state.

2. Aluminum coated E-glass fibers are further reduced in strength upon being infiltered by molten aluminum to produce aluminum-fiber composites.

3. The strength of longitudinally oriented fiber composites obeys the equation

$$S_c = V_f \times S_f + (1-V_f) S_m$$

where V_f = volume fraction of fibers

S_f = strength of fibers

S_m = strength of metal (believed to be flow or yield strength, but data not good enough to distinguish)

4. Short fibers do not contribute strength beyond that expected for equivalent dispersed particle hardening.

5. Vapor coating fibers with unreactive metals (barrier coatings) provides protection from attack during the process of compact manufacture. The strength of barrier coated fibers "in situ" in compacts equals the strength in the uncoated stage prior to treatment.

6. The ductility of compacts in which the fibers are oriented at about 45° to the tensile axis is about 5% and the strength of such compacts is about the same as the longitudinally oriented fiber compacts. The yield strength (0.2%) is much higher than that for the unreinforced metal.

APPENDIX I

ENHANCING DUCTILITY OF FIBER-METAL COMPOSITES:

In the course of making non-metallic fiber-metal composites it was discovered that the ductility of the composite produced by this method was a function of the orientation of the fibers relative to the principal stress axes. Ductility is a measure of the plasti flow that occurs in the specimen on being stressed to failure. In a tensile test it is measured by either the elongation

to fracture or the reduction in area at the fracture section. It was discovered that when the fibers were oriented parallel to a principal stress direction the elongation to fracture and the reduction in area was nil -- that is, the specimens were brittle. However, when the major fraction of the fibers were oriented at an appreciable angle to the principal stress axes (on the order of 45^{o}) than the specimen elongated by a sufficient amount prior to fracture to be able to pass many design specifications for minimum non-zero ductility. Further, the strength of such composites were almost as high as the strength of the parallel oriented fiber composites. This result, which was entirely unsuspected, markedly increases the applicability of the fiber-metal composites and removes the main disadvantage to the application of these composites as structural parts.

If the fibers are randomly oriented, then it was discovered that there is some increase in ductility relative to a parallel oriented fiber composite. However, the increase was not as large as could be obtained when all the fibers are optimally oriented. That is, it was found that if all the fibers are oriented at the same optimum angle relative to a principal stress axis, within a range of angle equal

$\pm 20^{o}$, then the ductility is appreciable without any important loss in strength. It was also found that if all the fibers are oriented 90^{o} to one principal stress axis than there is appreciable ductility but no important strengthening relative to the strengthening that can be achieved if the fibers are all oriented parallel to that stress axis.

That is, the maximum strengthening occurred with parallel fibers; the maximum ductility with perpendicular fibers.

The application of these concepts to the design of a composite material for a structural application is as follows. The specifications for the use of a material in any particular application usually specify a minimum ductility and a minimum strength. The principal stresses in the application are generally known. Knowing the curves showing tensile elongation as a function of the volume concentration of fibers orientation and fiber concentration that will satisfy the minimum specifications. Thus, from these considerations it is apparent that no particular fiber orientation can be specified which will be applicable for all applications. However, it is also apparent that choice of a fiber orientation of 45^{o} relative to all tensile principal stress directions will usually

satisfy most conditions.

It should be noted that all the fibers need not be oriented in the same direction to satisfy the ductility condition. If only one of the three principal stresses is in tension, then the fibers can be oriented at any direction that is at the desired angle to the principal stress axis. In this case if all the fiber directions passed through one point they would generate a cone with a half angle of the said desired angle, and an axis parallel to the principal stress axis. If two principal stresses are in tension, then the orientation of the fibers depend upon the properties desired. An anisotropic sheet material can be produced by aligning a portion of the fibers along one direction and the remaining portion along a direction nearly perpendicular to the first, both of which directions lie in the plane determined by the two principal stresses (the plane of the sheet for sheet material). In this anisotropic material the ductility of the fiber directions will be nil and increase to a maximum in some other direction between the two fiber directions. However, an isotropic ductile sheet material can be made by having no fiber direction in the plane of the sheet. As will be described later, this can be achieved by

the stacking of helically wound cylinders of fibers, alternate layers having nearly perpendicular intersecting cylinder axes or by the weaving of helically wound cylinders of fibers, or by the stacking of alternate layers in which short fibers lie at 45° to the plane of the sheet of helically wound cylinders of fibers, and in which the line of intersection of the plane that contains the fibers and is 45° to the sheet with the plane of the sheet is rotated by 90° on progressing from one layer to the next in the stacking of layers.

A method of producing the desired fiber directions in a cylindrical part requiring uniaxial strength and ductility is to wind the fibers about the axis in a double helix (a right hand and a left handed helix), much as the way a spool of thread is wound on a core. In both cases the helix angle is at the desired value. In the latter case, the resistance to shear between alternate helices is greater than in the former case with consequent loss in ductility. However, the ductility in both of these cases is likely to be low. In one particular case, for a singularly wound helix of continuous fiber (6% by volume) in a tin matrix, an elongation

to fracture of 4% was obtained at a tensile strength of 14,000 psi.

Another method is to use fibers which are longer than about one centimeter and which are stacked in the desired directions by oriented feeding and stacking of the fibers either along helical surfaces or conical surfaces oriented at the desired angle relative to the specimen axis.

REFERENCES:

1. D. L. McDanels, R. W. Jech, and J. W. Weeton. A.S.M. Fall Meeting, 1959.

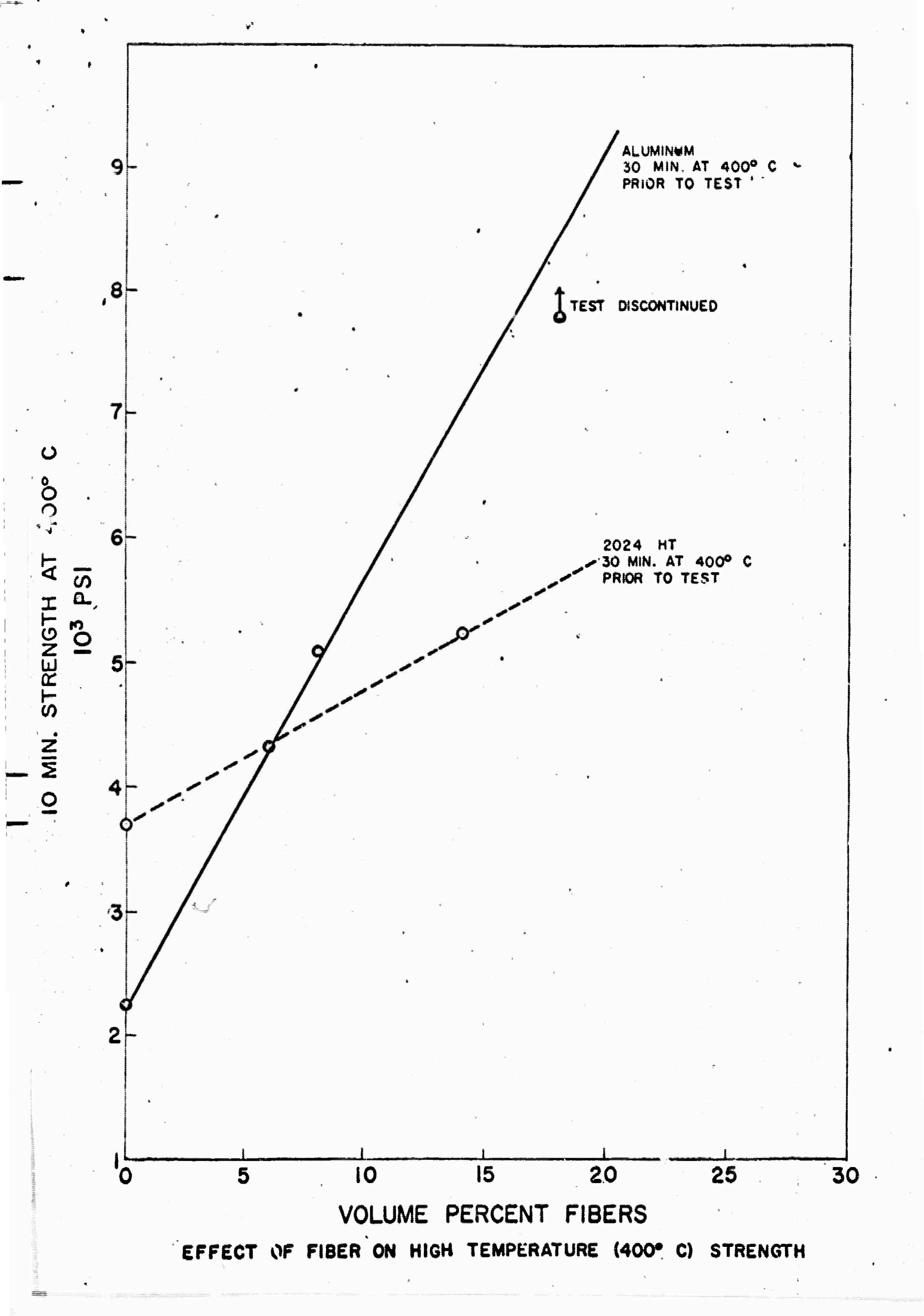
TABLE I

FIBER PROPERTIES

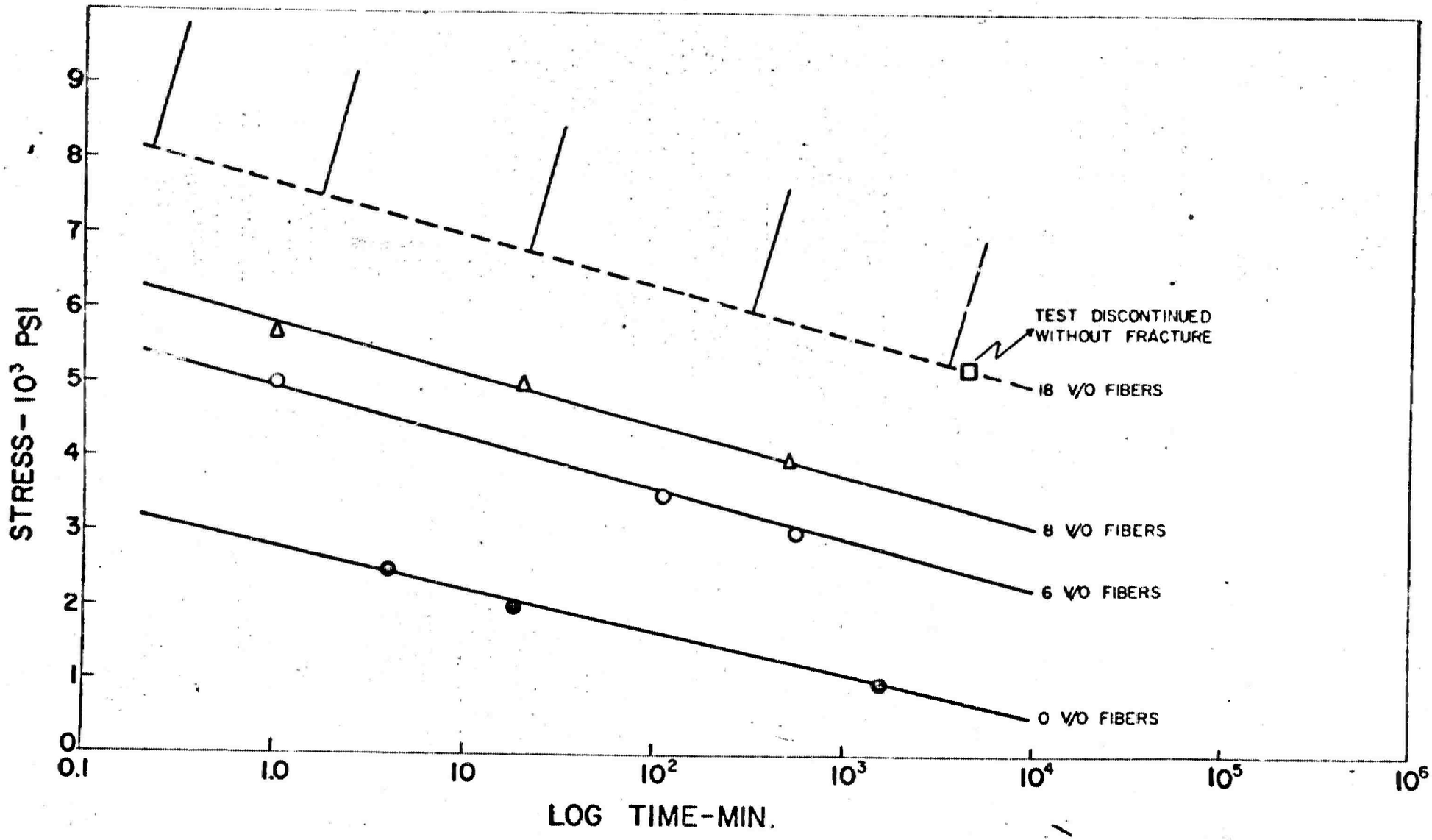
FIBER	STRENGTH PSI	SOFTENING TEMPERATURE °F	SPECIFIC GRAVITY	COEFFICIENT OF THERMAL EXPANSION in/in/°F
E-glass	690,000	1700°F	2.53	2.33×10^{-6}
Fused Quartz	250,000	2000°F	2.20	0.31×10^{-6}
Fiberfrax	180,000	3240°F	2.73	3.44×10^{-6}
Kaowool	420,000	3240°F	2.70	3.44×10^{-6}
Pyrex wool	406,000	932°F	-	1.67×10^{-6}

TABLE 2

	Tin	Tin + 6% Fibers (45°)
Yield Strength (0.2%)	1,300	9,300
Tensile Strength	2,200	13,600
Elongation (%)	45.0	4.0



EFFECT OF FIBER ON HIGH TEMPERATURE (400° C) STRENGTH



STRESS RUPTURE CURVES FOR AS CAST ALUMINUM AT 400° C WITH LONGITUDINALLY ORIENTED "E GLASS" FIBERS.

FIGURE 2